# Preparation of Nanocrystalline Titanium Oxide by Decomposition of Molecular Precursor $\alpha$-$(NH_4)_2TiO(SO_4)_2$

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Hydroxy-free anatase $TiO_2$ nanocrystals (25 nm) with photocatalytic activities higher than that of commercial photocatalyst Degussa P-25, were prepared by nonhydrolytic thermolysis of ammonium titanyl sulfate at 700 °C for 2 h.

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Nanocrystalline metal oxides are of considerable interest for a wide variety of applications, ranging from electronics via ceramics to catalysts, because of their unique or improved properties. Their properties are primarily dependent on particle size, composition, structure and synthetic process. The solution-phase chemistry used to make nanocrystalline oxides in particular titania, employes hydrolysis of metal alkoxides or halides.[1–4] Nanocrystals obtained from wet chemistry route have fully hydroxylated surfaces unless extreme heat treatments or chemical dehydroxylation reactions are applied, and these hydroxyls influence material properties.[1] At present, a synthetic process that can rapidly and continuously produce diverse materials of nanometer size, with well-defined compositions, crystallinity and structures, is still to be a challenge. Recently, thermal decomposition of ammonium aluminum carbonate hydroxide and zinc peroxide was used to prepare nanocrystalline $\alpha$-$Al_2O_3$[5] and ZnO,[6] respectively. Salt-assisted aerosol decomposition was applied to prepare other oxides with high specific surface area,[7] and solution-based nonhydrolytic methods have been developed for successful synthesis of nanocrystalline $TiO_2$ in the presence of organic compounds as solvent or surfactants.[8,9] However, the organic compounds may be undesired for many applications. In this communication we describe nonhydrolytic preparation of titania nanocrystals using the thermolysis of ammonium titanyl sulfate, which should be similarly applicable to many nanocrystalline metal oxides. This method clearly yields materials with properties being distinct from those prepared by precipitation methods, leads to a less expensive product and makes these materials technologically more interesting.

For the synthesis of the double salt $\alpha$-$(NH_4)_2TiO(SO_4)_2$, 200 g of $Ti(SO_4)_2$ was dissolved in 400 mL of distilled water, then 102 g of $(NH_4)_2SO_4$ was added into the above solution. The clear solution was placed undisturbedly. A white precipitate was separated out after 3 days aging. A bulk amount precipitate was obtained (yield up to 40%) after prolonging the time for aging such as 15 days. When 3 M $TiOCl_2$ solution was used as titanium source instead of equimolar $Ti(SO_4)_2$, the phase of the obtained white precipitate matched with that derived from $Ti(SO_4)_2$, identically both assigned to $\alpha$-$(NH_4)_2TiO(SO_4)_2$ (JCPDS 34-0732). 5 g of ammonium titanyl sulfate was placed in a high-purity quartz boat and set in a quartz tube furnace (inner diameter 82 mm) with air-tight end gaskets. The reactor was flushed with air to eliminate $SO_3$ in the system during the thermolysis of ammonium titanyl sulfate and the releasing $SO_3$ was absorbed by water. Then, the precursor was heated to an appropriate temperature and held for 2–8 h to obtain $TiO_2$ powder.

Figure 1 shows XRD patterns of the as-prepared molecular precursor $\alpha$-$(NH_4)_2TiO(SO_4)_2$ and its calcined products at varying temperatures in air. The names of calcined samples were abbreviated as A6002, A7002 and AR9002, where A and R represent anatase and rutile respectively, the digit 600 denotes the calcining temperature at 600 °C while the digit 2 denotes the calcining time for 2 h. A6002 consists of major anatase $TiO_2$ and a small amount of orthorhombic $TiOSO_4$, suggesting that the precursor was partially converted into $TiO_2$ at this temperature for 2 h. The complete conversion is achieved by prolonging the calcining time or raising the calcining temperature. For example, Figure 1c shows the XRD pattern of A7002, which consists of pure anatase titania nanoparticles. The powder A6008 is also only comprised of anatase nanocrystals. The product AR9002 is dominantly composed of rutile (79.4%), owing to the anatase-to-rutile transformation.

Figure 2 shows TEM images of some products. The products A6002, A7002 and AR9002 are in the size of 15–20 nm, 20–30 nm and 80–100 nm, respectively. Correspondingly, the specific surface areas of these samples are 61.6, 64.5 and 7.0 $m^2/g$. The specific surface area of A6002 is lower than that of A7002 because of the existence of $TiOSO_4$ in micrometer-size, which has little contribution to the specific surface area. It is notable that the surface area of A7002 and

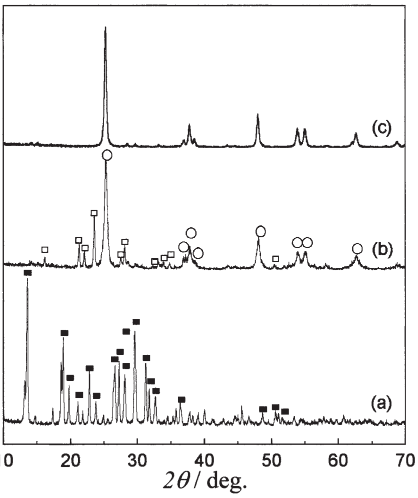

**Figure 1.** X-ray diffraction patterns of (a) $(NH_4)_2TiO(SO_4)_2$ (b) A6002 and (c) A7002. The XRD peaks indicated by (■), (□) and (○) were attributed to $\alpha$-$(NH_4)_2TiO(SO_4)_2$, orthorhombic $TiOSO_4$ and anatase $TiO_2$, respectively.

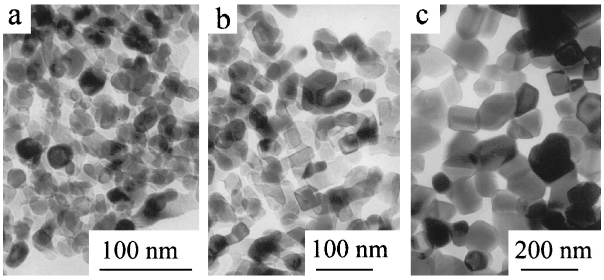

**Figure 2.** TEM images of (a) A6002, (b) A7002 and (c) AR9002.

AR9002 is relatively higher than that of titania powders derived from wet chemical methods under such high temperature annealing. Sibu et al.[10] reported that the specific surface area of their titanium oxide after calcination at 700 °C was 1 m$^2$/g, and could be increased to as high as 52 m$^2$/g in the presence 1% $La_2O_3$. Other methods to keep high stability of $TiO_2$ nanoparticles against particle growth include the formation of a metastable solid solution on the surface of oxide nanoparticles[11] or the replacement of the surface hydroxyl groups with another functional group.[12] Neither dopants nor additives are introduced into A7002 and AR9002, however, they still retain remarkably high surface area.

The whole reaction of the thermolysis of $(NH_4)_2TiO(SO_4)_2$ can be expressed as:

$$(NH_4)_2TiO(SO_4)_2(s) \rightarrow TiO_2(s) + (NH_4)_2SO_4(s) + SO_3(g) \tag{1}$$

Though $(NH_4)_2SO_4$ is in the solid state in eq 1, the white powder of $(NH_4)_2SO_4$ is deposited at the cool end of the quartz tube in practical reaction. In other words, gaseous $NH_3$ and $SO_3$ rather than solid $(NH_4)_2SO_4$ are produced in the quartz boat during its thermolysis. So, no impurity in $(NH_4)_2SO_4$ is detected by XRD and FTIR. Both the releasing gases and the absence of water thus less hydroxyl group available for the particle growth[12] are favored to retain relative fine size and high thermal stability of the resultant $TiO_2$ powders.

Figure 3 shows the FTIR patterns of $TiO_2$ powders after calcination at 700 °C for 2 h, one was prepared according to our previous work,[13] the other was A7002. The peaks at 3350–3450 cm$^{-1}$ and 1620–1630 cm$^{-1}$ are assigned to the stretching vibrations of OH groups and bending vibrations of adsorbed molecular water, respectively. The fact that no vibration frequencies assignable to S–O band is observed illustrates the high purity of A7002. The peak intensity for OH groups of A7002 is greatly decreased to almost zero, indicating the less hydroxylated characteristic of this powder.

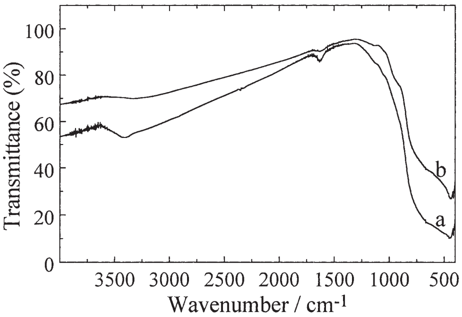

**Figure 3.** FTIR spectra of anatase $TiO_2$ (a) derived from wet chemical precipitation after calcination at 700 °C for 2 h and (b) A7002.

**Table 1.** Comparison of the photocatalytic properties of A7002 with P-25 in the degradation of phenol solution

| | Degradation efficiency (%) for the various time | | | |
|---|---|---|---|---|
| Catalyst | 15 min | 30 min | 60 min | 90 min |
| P-25 | 47.6 | 74.2 | 98.7 | 99.5 |
| A7002 | 66.6 | 86.7 | 99.2 | 100 |

The photocatalytic activity has been tested in the photodegradation of aqueous solutions of phenol and evaluated by comparison with Degussa P-25, which consists of 80% anatase and 20% rutile and has a specific surface area of 50 m$^2$/g. The setup of photocatalytic reactor and conditions is the same as that of our published work,[13] but $O_2$ was bubbled into aqueous suspensions at the flow rate 100 mL/min in the present work. As shown in Table 1, the photocatalytic activity of A7002 is higher than that of Degussa P-25. P-25 is believed a commercial photocatalyst with high photocatalytic activity due to the synergetic contribution by the mixing of anatase and rutile[14] and the suppressing of the recombination of photogenerated electron-hole pairs by doping small amount of Fe(III) ions.[15] The higher photocatalytic activity of A7002 suggests the high crystallinity as well as the easily dispersing ability in water.

In summary, less hydroxylated $TiO_2$ nanocrystals in the size of 20–30 nm were synthesized by a thermolysis route and such high-temperature processing may be ideal for producing fully crystallized $TiO_2$ with higher thermal stability than that derived from low-temperature wet-chemical route. In photocatalytic degradation of phenol reaction, hydroxyl-free $TiO_2$ nanoparticles without $Fe^{3+}$ doping show higher photocatalytic activity than Degussa P-25 produced by the flame process.

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